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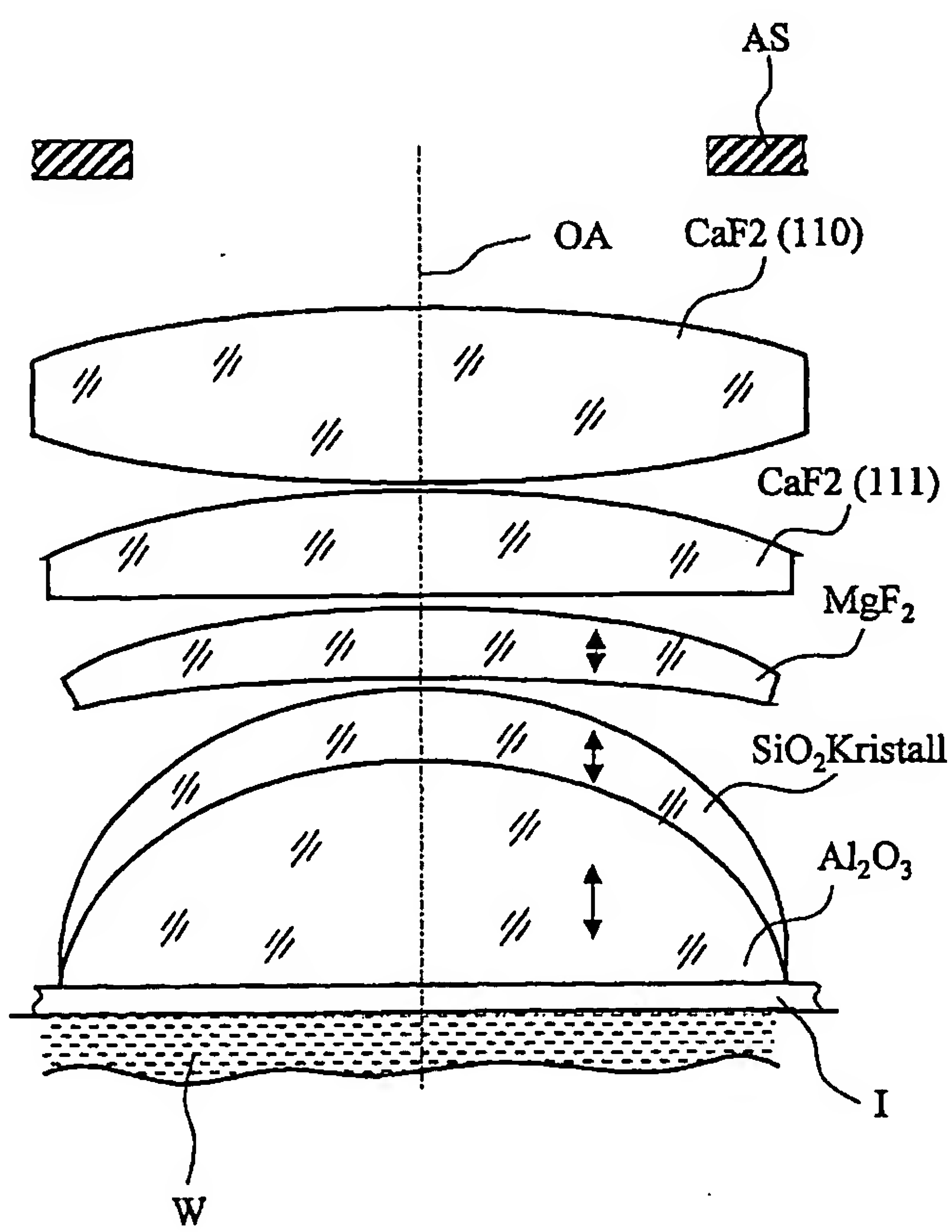
(54) Title: MICROLITHOGRAPHY PROJECTION OBJECTIVE WITH CRYSTAL ELEMENTS



(57) Abstract: A microlithography projection objective is proposed with optical elements, i.e. lenses or planar-parallel plates (used as end-closure plates) of crystalline magnesium fluoride, quartz, lanthanum fluoride, sapphire and Alpha-aluminium oxide. Suitable crystallographic orientations, crystal 10 combinations, and polarizations of the light are described. Suitable applications are for immersion lithography or near-field lithography in the DUV and VLN range, using the highest numerical aperture values.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Microlithography Projection Objective with Crystal Elements

The invention relates to a microlithography projection objective with crystal elements, namely such made from materials showing birefringence and other than cubic crystal structure.

These are of relevance mainly as some of them show refractive indices well above those of quartz glass or calcium fluoride, what is a substantial need for immersion lithography with image side numerical apertures beyond 1.0 up to about 2 or more.

From publications such as

Bruce W. Smith et al. Optical Microlithography XVII Proc. SPIE 5377 (2004), p 273 -284;

Bruce W. Smith et al. Optical Microlithography XVI, Proc. SPIE 5040 (2003), p 679 -689;

John H. Burnett et al. "High Index Materials for 193 nm and 157 nm Immersion lithography"
Int`l Symp. on Immersion & 157 nm Lithography, Vancouver 8/2/04 (NIST/ Corning Tropel)

and patent applications such as
WO2004/019 128 A2,
or, commonly owned with this application:
US 6,717,722 B,
US Ser. No. 10/734,623 filed 15 Dec. 2003,
US Ser. No. 60/530,623 filed 19 Dec. 2003,
US Ser. No. 60/530,978 filed 22 Dec. 2003,
US Ser. No. 60/544,967 filed 13 Feb. 2004,
US Ser. No. 60/568,006 filed 04 May 2004,
US Ser. No. 60/592,208 filed 29 July 2004,
US Ser. No. 60/591,775 filed 27 July 2004,
US Ser. No. 60/612,823 filed 24 Sept 2004,
DE 10 2004 051 730.4 filed 22 Oct. 2004

some information about this art can be gathered.

Of these, e. g. WO 2004/019 128 A2, US 10/734,623, US 60/592,208, US 60/591,775 and US 60/612,823 show objective designs which can be optimized by and combined with the use of materials and teachings according to this application.

Suitable immersion liquids are inter alia described in US 60/568,006 or DE 10 2004 051 730.4.

All cited documents are incorporated into this application by reference in their entirety.

Their citation in no way constitutes any declaration on their relevance for this application, and the list certainly is incomplete and many more publications relate to this art.

□

For end-closure plates or for the last-positioned lens element in immersion objectives or near-field objectives there is a need for optical materials of the highest possible index of refraction. At the same time, the materials need to be transparent, homogeneous, radiation-resistant, as well as mechanically and chemically robust. There is a material which meets all of these conditions except for optical isotropy. The material is sapphire or, in chemical terms, Al_2O_3. Others are MgF_2 or LaF_3 and other uniaxial crystals.

In an absolutely telecentric light path and with completely tangential polarization it is possible to achieve complete isotropy of the light-transmitting properties by using the measures proposed by the present invention.

The claims together with this specification describe solutions to these problems and advantageous varieties.

Figures 1 to 8 and 10 to 13 are sketches that illustrate the principles of arrangements, or parts thereof, according to the invention.

Figure 9 shows wavelength-dependent variation of n_e and n_o for some materials from an article.

In the illustrated arrangements, for example in Figure 2, the sum $(n_o-n_e)Al_2O_3$ + $(n_o-n_e)SiO_2$ equals zero for a maximum-aperture

ray B_{max} with an incident angle of 70° (n_o refractive index of ordinary ray, n_e refractive index of extraordinary ray).

The following symbols are used in the drawings:

AS = aperture stop / system aperture
P = protector plate / protective element
I = immersion fluid, immersion
W = wafer, or the object to be exposed in the image plane
OA = optical axis
L = lens
B_{max} = ray of maximum aperture

With tangential polarization of the light rays there is only one component, namely the p-component, and as a consequence, there is no phase shift between p- and s-components as long as the optical crystal axis of the crystal is oriented in exact parallel alignment with the optical axis of the objective. However, these conditions are met only approximately in practical cases. As a means to achieve perfect isotropy in the effect that a plate of this kind has on light rays, it is proposed according to the present invention that the plate be made of two parts. The proposed combination consists of an Al_2O_3 sapphire plate P_1 of optically negative character and an SiO_2 crystal plate P_2 of optically positive character, as illustrated in Figures 1 to 3. The magnitude of the birefringence changes individually with the wavelength. The plate thicknesses are therefore selected dependent on the wavelength, so that a birefringence of the Al_2O_3 plate is compensated by the complementary birefringence of the SiO_2 plate. This cannot be achieved completely, because the indices of refraction are different for the two materials, so that a compromise is necessary for different incident light angles. However, an exact compensation can be

achieved in particular for the highest apertures which are relevant in immersion lithography applications, e.g., for dipole illumination.

In addition to a planar plate, the invention can also be used in a lens element. Since Al_2O_3 sapphire offers one of the highest known indices of refraction for the wavelengths of 157 nm and 193 nm, it is a preferred material to use for the element in the last position of the objective. Elements of crystalline SiO_2 are placed (in direction of light propagation) before the Al_2O_3 element.

Figure 4 represents a sketch to illustrate the principle, wherein the symbol QG stands for quartz glass, QK for quartz crystal, S for sapphire (which is at the same time a lens L in the sense of Figure 1).

It also makes sense to use arrangements of elements that are joined together by wringing. The fact that the absolute amount of birefringence is larger in crystalline quartz is of practical significance because less of the SiO_2 crystal is needed for compensation. Also, crystalline SiO_2 has the smaller index of refraction and its use at the image-oriented end of a high-aperture immersion objective is therefore less advantageous.

An arrangement that is suitable for example for a wavelength of 193 nm is shown in Figure 5. The spaces between the lenses, particularly in the area near the image plane where there are large ray angles relative to the optical axis, can be filled by high-refractive fluids FL1 of the same kind that are also used as an immersion medium. A double arrow in the lenses indicates the orientation of the optical axis of the birefringence that is inherent in the materials.

It is clear that the effective index of refraction in the crystals Al_2O_3 and SiO_2 is subject to a continuous angle-dependent variation, but with tangentially polarized light there is initially no phase shift between an s-polarized and a p-polarized component. The variation of the refractive index is taken into account in the design.

Figure 6 illustrates an example of an objective for an operating wavelength of 157 nm with CaF_2 lenses of different crystallographic orientation, for example 111 and 110, for the compensation of intrinsic birefringence with a pair of optically uniaxial crystal lenses that is compensated in accordance with the invention. With immersion I or the near-field lithography technique, the objective can be coupled to the object to be exposed, for example a wafer W, with the largest possible numerical aperture.

Because of the high light-gathering power (etendue), it is preferred to make the compensation. This is the best way to master the problem of extended fields outside of the telecentric light path without the split between s-polarization and p-polarization. Of course, with a skewed incident radiation in birefringent crystals, the n_e-components run outside the plane of incidence. However, with the different character of SiO_2 crystal and Al_2O_3 sapphire, it is possible to take specifically targeted countermeasures.

The term "negative optical character" means that the refractive index n_o of the ordinary ray is larger than the refractive index n_e of the extraordinary ray.

The term "positive optical character" means that the refractive index n_o of the ordinary ray is smaller than the refractive index n_e of the extraordinary ray.

The scope of the invention includes: the compensation as described; the use of Al_2O_3 sapphire and SiO_2 crystal in lithography optics; the placement of the elements between the aperture stop or a conjugate location of the aperture stop and the image plane of a projection objective, with special preference for placing these elements in the bottom one-third of the distance between the aperture stop and the image plane; the use of the aforementioned materials for protector plates for immersion or near-field arrangements, either by themselves without compensation, or with compensation; the use at high angles of incidence >60°, with special preference >70°; including in these applications the compensation at the highest numerical aperture values NA (above 1.3 to 1.6) on the image side; also including the use of tangentially polarized light; and further including the use in immersion objectives with a refractive index of more than 1.8 in the last optical element, with special preference for more than 2.0; and also the use at an operating wavelength of 157 nm in conjunction with the crystals CaF_2, SiO_2, Al_2O_3 sapphire - in respectively different combined arrangements.

Similar to silicon dioxide, magnesium fluoride in crystalline form has an optically positive character. The advantage of MgF_2 lies in its high UV transmittance, particularly at 157 nm. Its drawback is the low coefficient of refraction, for example at a wavelength of 193.304 nm, with values of n_o = 1.427460 and n_e = 1.441069.

The compensation of birefringence in a high-aperture end-closure part of a microlithographic projection objective .

requires the availability of suitable degrees of freedom. If the birefringence were of exactly equal magnitude and had the same form in Al_2O_3 as in quartz crystal, an exact solution that provides compensation for all angles would exist at least for planar-parallel plates, i.e., one would only need to use two plates of equal thickness. If lenses are used instead of plates, the possible phase differences occurring as a result of refraction and birefringence become larger and there is an increased risk that this will affect the image quality. On the other hand, with lenses one has the possibility to use a targeted variation of the radii as a further degree of freedom in addition to the thickness, as a parameter for compensation.

Based on these considerations, a further material is proposed for an additional fine correction, namely MgF_2 crystal. In view of its low index of refraction, it is placed preferably in a position before the more strongly refractive elements of quartz crystal and sapphire. It should be noted in this context that the uniaxial birefringent crystals Al_2O_3 sapphire, SiO_2, MgF_2 are compensated in an entirely different manner than the CaF_2, SrF_2, and BaF_2 crystals and the like which are a priori isotropic (at least in the visible range).

The refractive index of the successive elements, for example at the 157 nm wavelength in the example of Figure 7, is continuously increased towards the wafer (image plane), namely up to a level of more than 2.0.

The optical path lengths for s-and p-polarization are largely equalized for the broadest possible range of angles through the simultaneous use of three crystalline materials Al_2O_3, SiO_2, and MgF_2. It should be noted that the harmful contributions for skewed rays increase the farther one moves

these elements away from the wafer, i.e., from the image plane. This also provides the special possibility of a compensation based on where a lens of each of the respective materials is positioned. The optical path length should to the greatest extent possible meet the condition $(n_o-n_e)Al_2O_3 \cdot d_1 + (n_o-n_e)SiO_2 \cdot d_2 + (n_o-n_e)MgF_2 \cdot d_3 = 0$, wherein n_o represents the refractive index for the ordinary ray, n_e represents the refractive index for the extraordinary ray, and d_1, d_2, d_3 represent the respective path lengths inside the crystals. It should be the aim (and it is possible) to meet the condition particularly well in the aperture angle range from 65° to 72°.

The scope of the invention likewise includes a lithography objective in a projection system, where the effect of birefringence of uniaxial crystal materials in end-closure plates or lenses on the image side of the objective is completely corrected for angles in the range from 65° to 72° (measured geometrically from the optical axis).

Instead of using Al_2O_3 sapphire for the compensation or as a provider for the primary refractive power in this end range, one could also use the uniaxial crystal material LaF_3 as a further possible lens material. Like Al_2O_3, it has a negative optical character and the birefringence values likewise resemble those of Al_2O_3. In comparison to sapphire, LaF_3 has the advantage that the commercially available crystals, which are made in a completely different manufacturing process, currently meet higher standards of optical quality. LaF_3 is water-insoluble, but it does not come up to the levels of hardness and UV transmittance of Al_2O_3 sapphire.

Figure 8 schematically illustrates an example for an operating wavelength of 193 nm where LaF_3 is used for the last

lens on the image side, in this case with a protector plate P of α-Al_2O_3. In this case, too, the alternative to an arrangement with an immersion fluid is an optical near field where the distance between the protector plate P and the wafer is shorter than the operating wavelength.

With this plate P of Al_2O_3 it is very important to pay attention to the fact that the α-modification of the crystal represents the advantageous choice. The γ-modification of Al_2O_3 is hygroscopic and should not be used.

Table 1:

Refractive indices of the uniaxial crystals

MgF_2		
wavelength	ordinary	extraordinary
248.338 nm	1.403248	1.416080
193.304 nm	1.427460	1.441069
157.629 nm	1.466666	1.481281

SiO_2		
wavelength	ordinary	extraordinary
248.338 nm	1.601568	1.612689
193.304 nm	1.660455	1.673963

Difference between indices $\Delta n = n_o - n_e$		
157.629 nm	Al_2O_3	0.012973
	MgF_2	0.014243

The birefringence values were measured by the interference method and are more reliable than measuring the indices n_o and n_e by means of prisms and taking the differences. In regard to this topic, reference is also made to an article in Applied Optics, March 1969, Volume 8 No. 3, p. 673, where the wavelength-dependent variation of n_e and n_o is discussed.

Figure 9 is copied from Fig. 3 of the aforementioned reference.

Further according to the invention, uniaxial crystals are compensated as follows:

Lenses LPP of positive refractive power and positive optical character are compensated by lenses LPN of positive refractive power with negative character (Fig. 10). In

addition, lenses of positive refractive power can also be compensated with lenses of negative refractive power with the same character, as shown in the example of Figure 11 - with positive character in the lenses LPP, LNP (negative refractive power), possibly supplemented by a lens LPN. Figure 12 shows an arrangement where lenses LPN, LNN, LPP follow each other, with LNN being a lens of negative refractive power and negative optical character.

As a further example, Figure 13 shows the four last lenses on the image side of a microlithography projection objective with the materials according to the invention as the significant mass (material) of the lenses, which may be coated with layers for antireflection, anticorrosion or the like (as in the other embodiments discussed), i.e., MgF_2 / SiO_2 crystal / optional fluid lens / LaF_3 / Al_2O_3 sapphire, and with appropriate compensation of imaging errors due to birefringence effects of the lens materials.

Patent Claims:

1. Microlithography projection objective with at least one lens of quartz crystal and with at least one lens of sapphire crystal.

2. Microlithography projection objective with at least two transmittent optical elements, in particular lenses (L) or planar-parallel plates (P) consisting of crystals that are uniaxial with regard to birefringence, wherein at least two of said optical elements consist of different crystal materials.

3. Microlithography projection objective according to claim 1 or claim 2, characterized in that an axis of birefringence of a first optical element and an axis of birefringence of a second optical element each run parallel to the optical axis of the geometrical light ray path inside the projection objective.

4. Microlithography projection objective according to at least one of the preceding claims, characterized in that said lenses (L) or optical elements (P) are arranged on the image side of a pupil or system aperture (AS) that is nearest to the image plane.

5. Microlithography projection objective according to at least one of the preceding claims, characterized in that said lenses (L) or optical elements (P) are among the three optical elements that lie closest to the image plane (W).

6. Microlithography projection objective according to at least one of the preceding claims, characterized in that

the numerical aperture on the image side is larger than 1.6 and with special preference larger than 1.8.

7. Microlithography projection system with a microlithography projection objective according to at least one of the claims 1 to 6.

8. Microlithography projection system according to claim 7, characterized in that polarized light passes through said crystalline lenses or crystalline optical elements.

9. Microlithography projection system according to claim 8, characterized in that the light is tangentially polarized.

10. Microlithography projection system according to claim 8, characterized in that the light is linearly polarized.

11. End-closure plate of a microlithography projection objective substantially made of α-Al_2O_3.

12. Use of an LaF_3 lens or LaF_3 planar-parallel plate in a microlithography projection objective.

13. Microlithography projection objective with at least two optical elements from the group that comprises lenses and planar-parallel plates substantially consisting of a material from the group that comprises crystals of MgF_2, SiO_2, LaF_3, sapphire, α-Al_2O_3.

14. Microlithography projection objective according to claim 13, characterized by the presence of two or three different materials selected from said group of crystals.

FIG.1

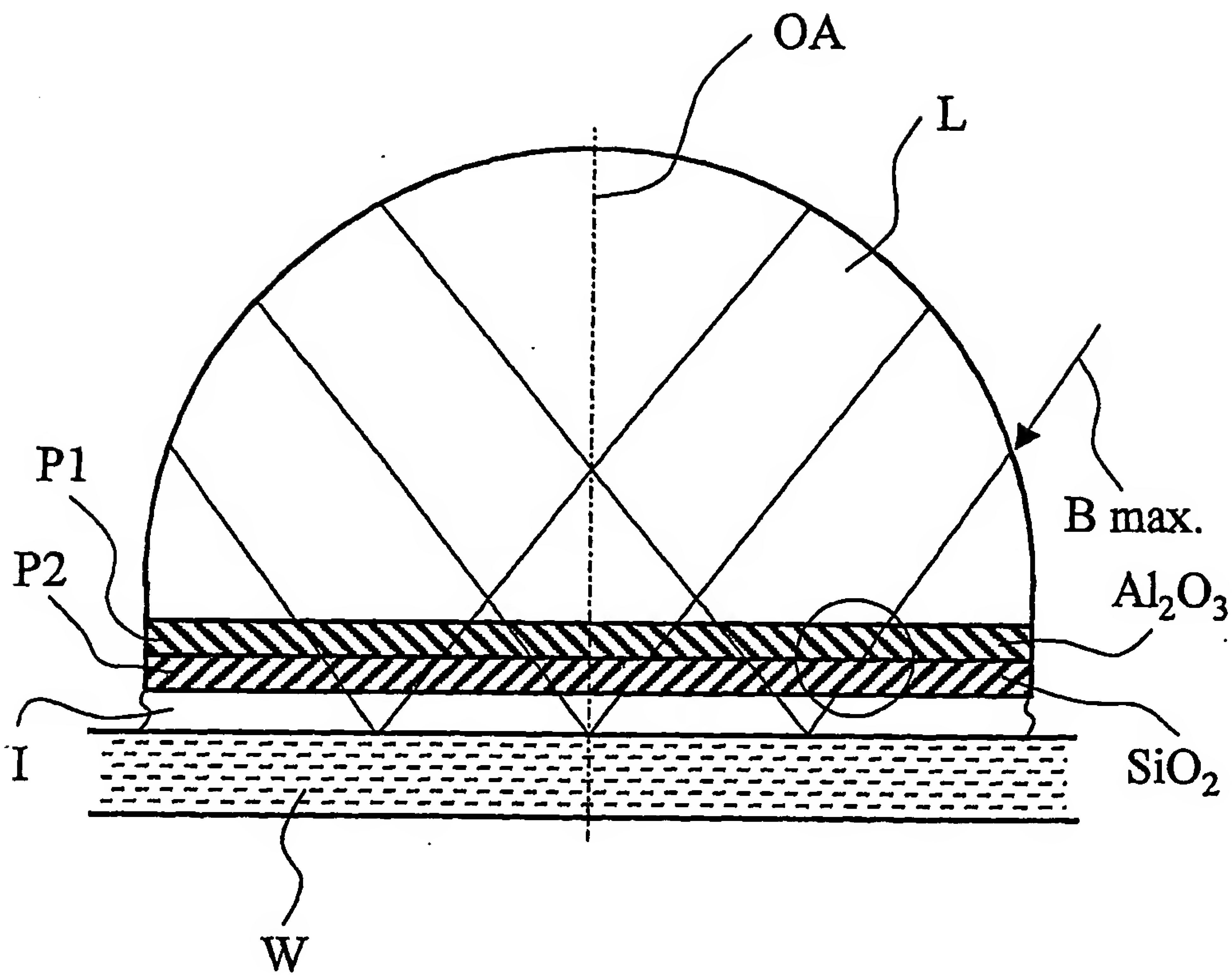


FIG.4

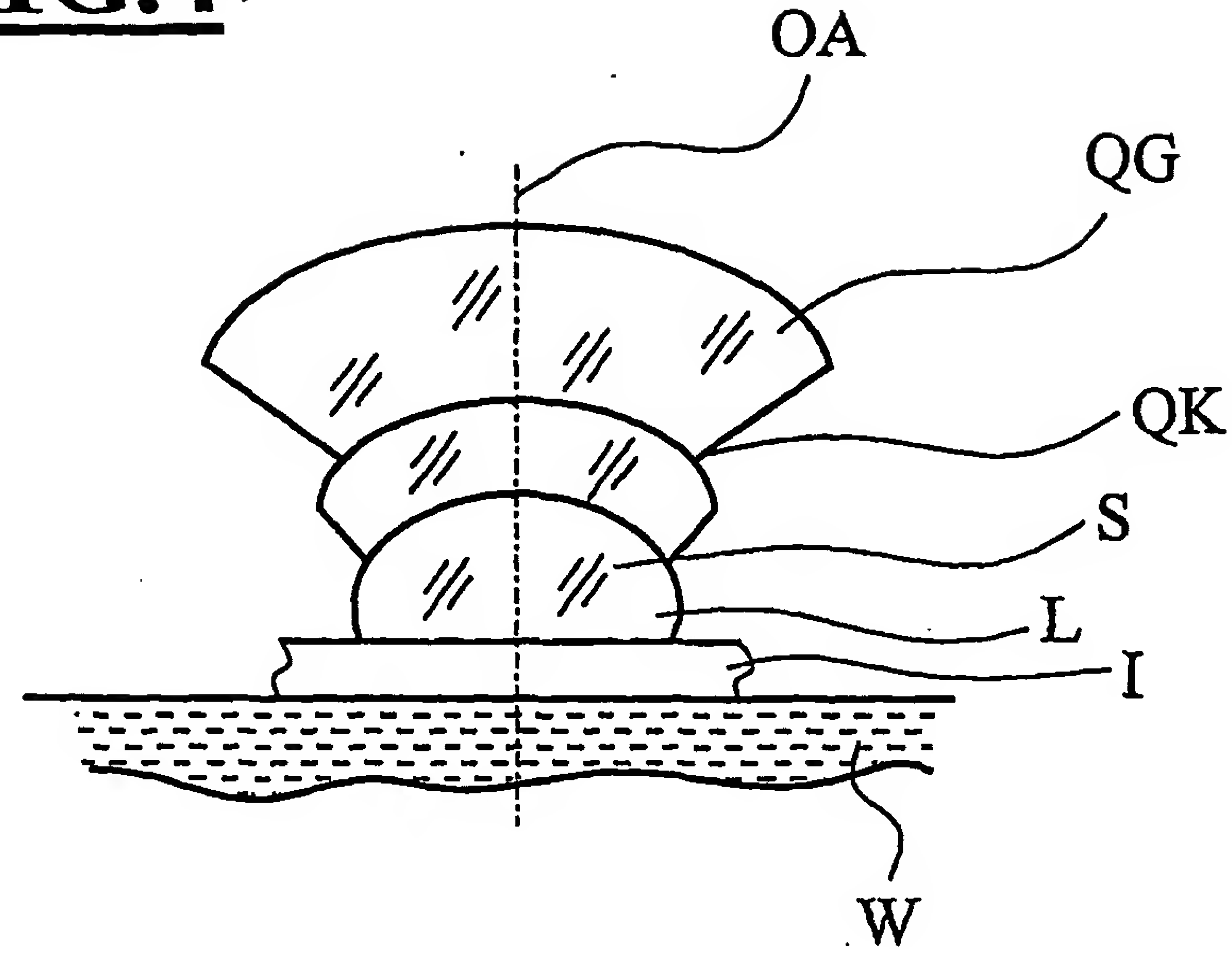


FIG.5

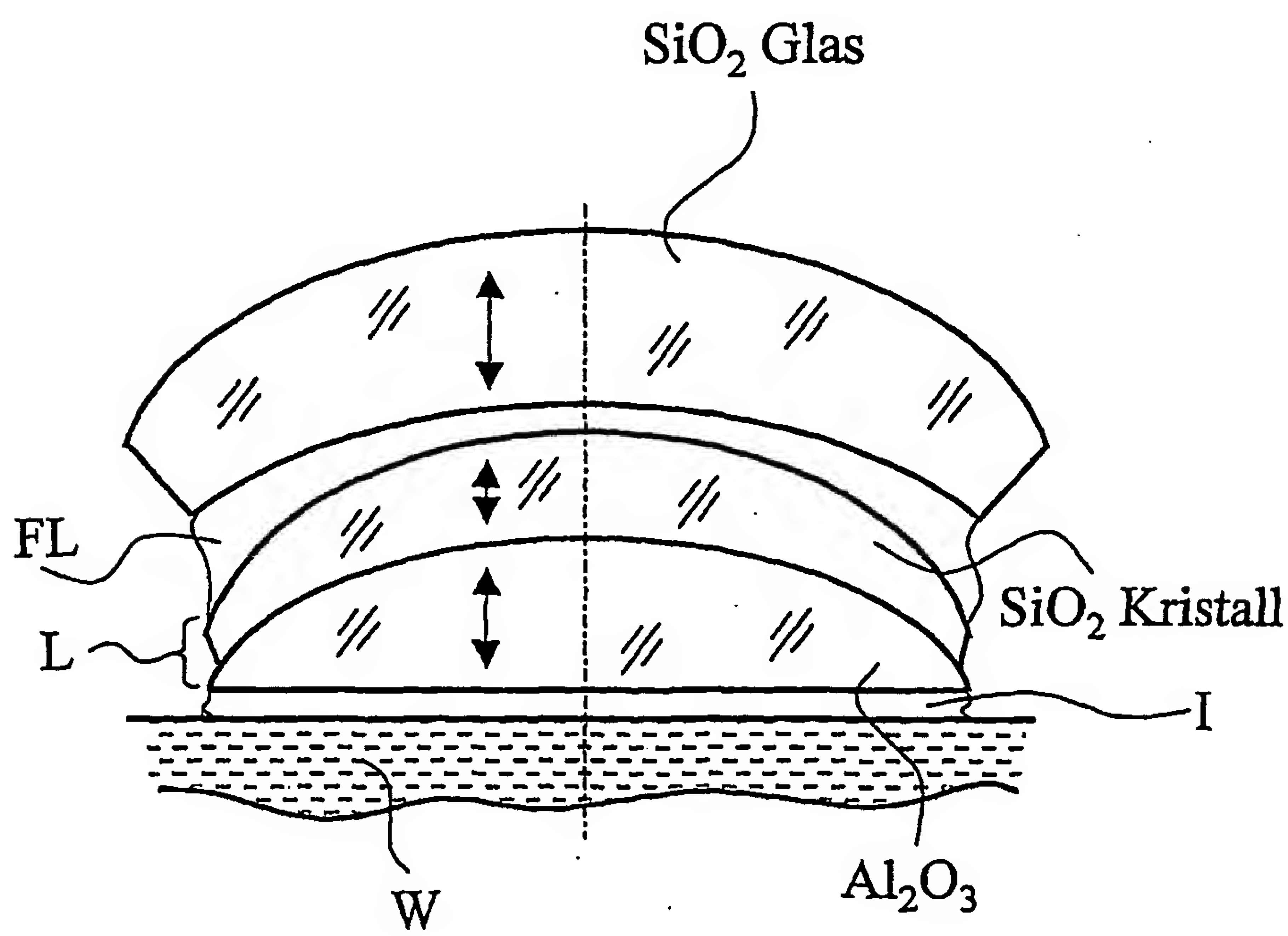


FIG.6

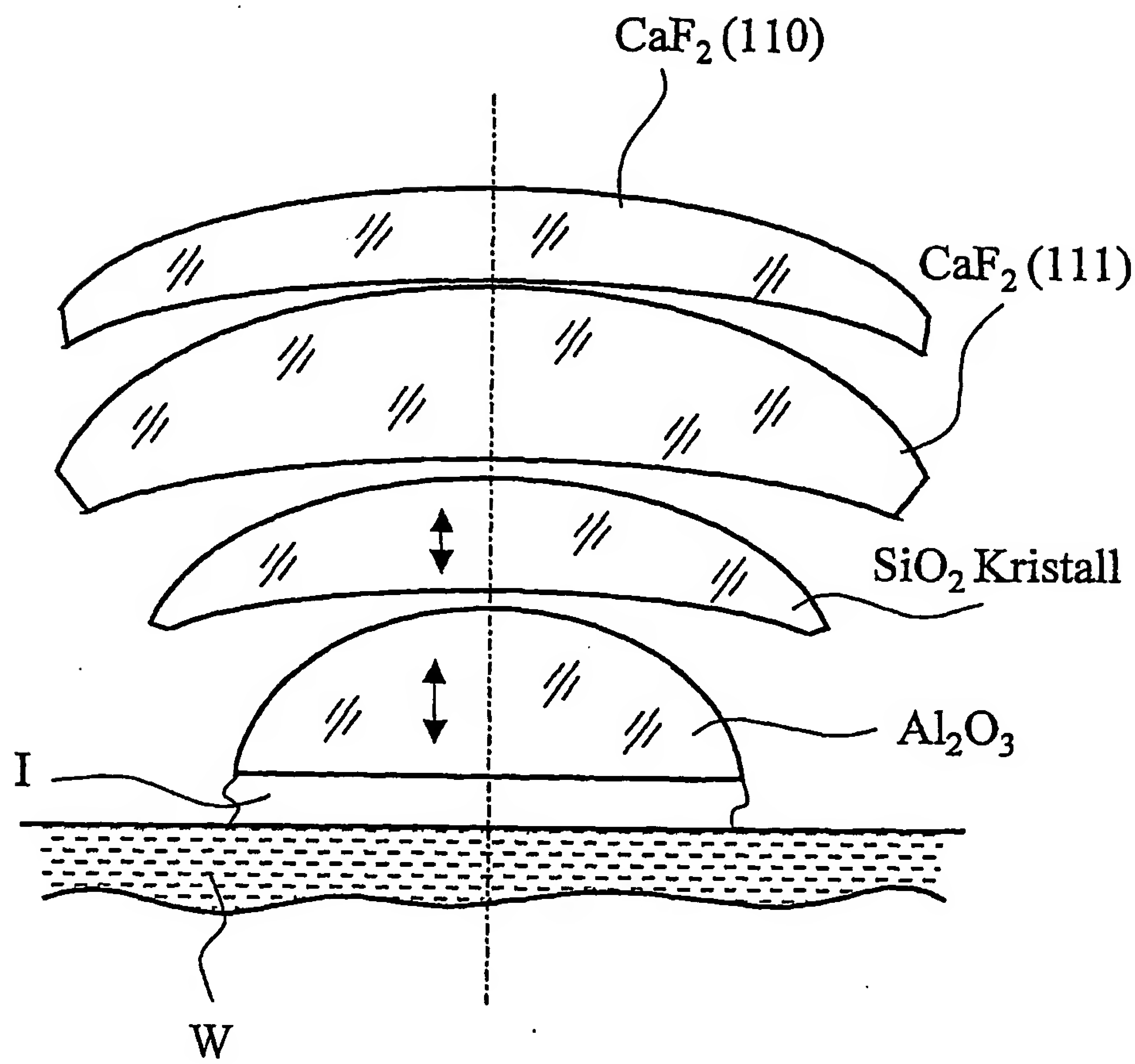


FIG.7

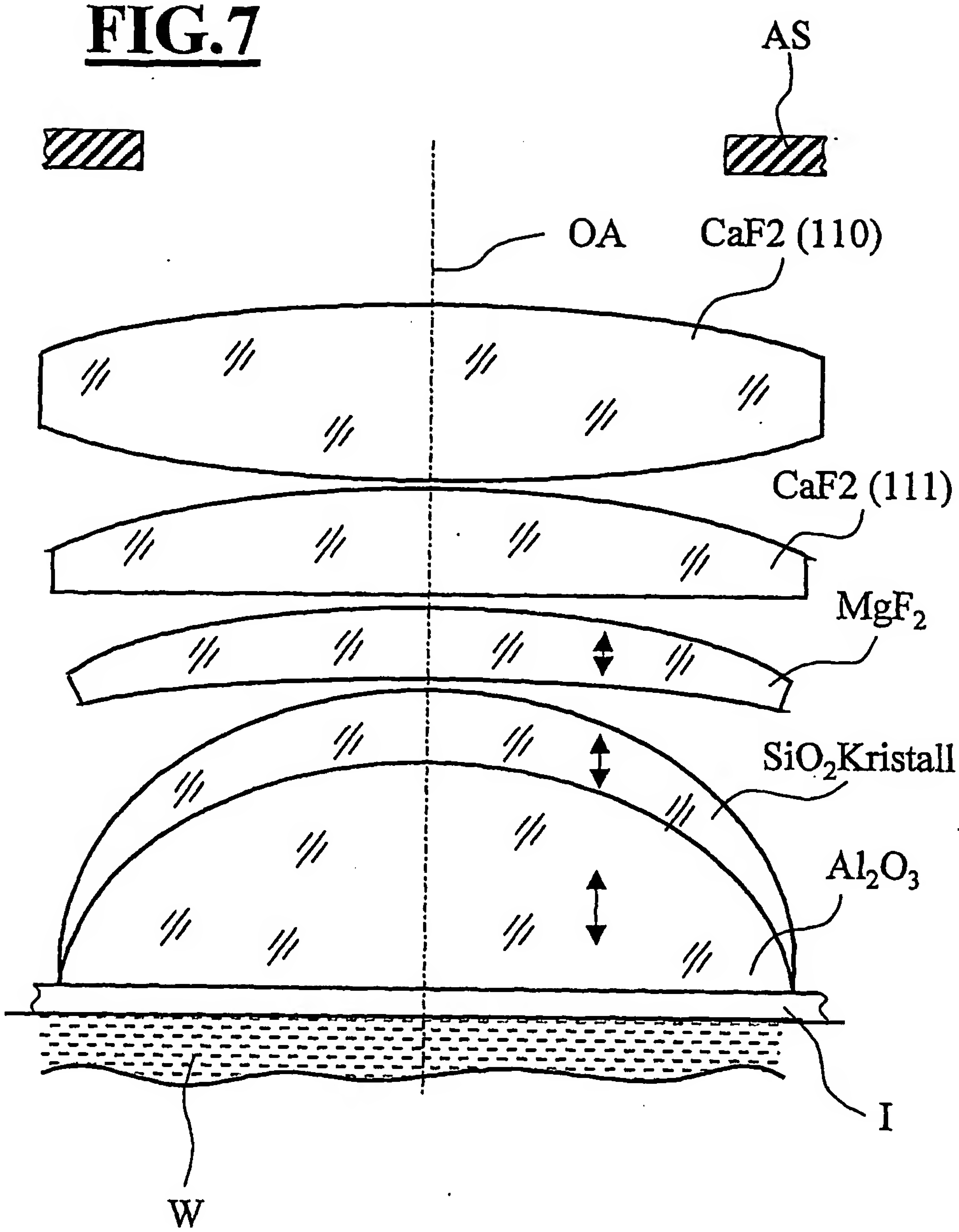


FIG.8

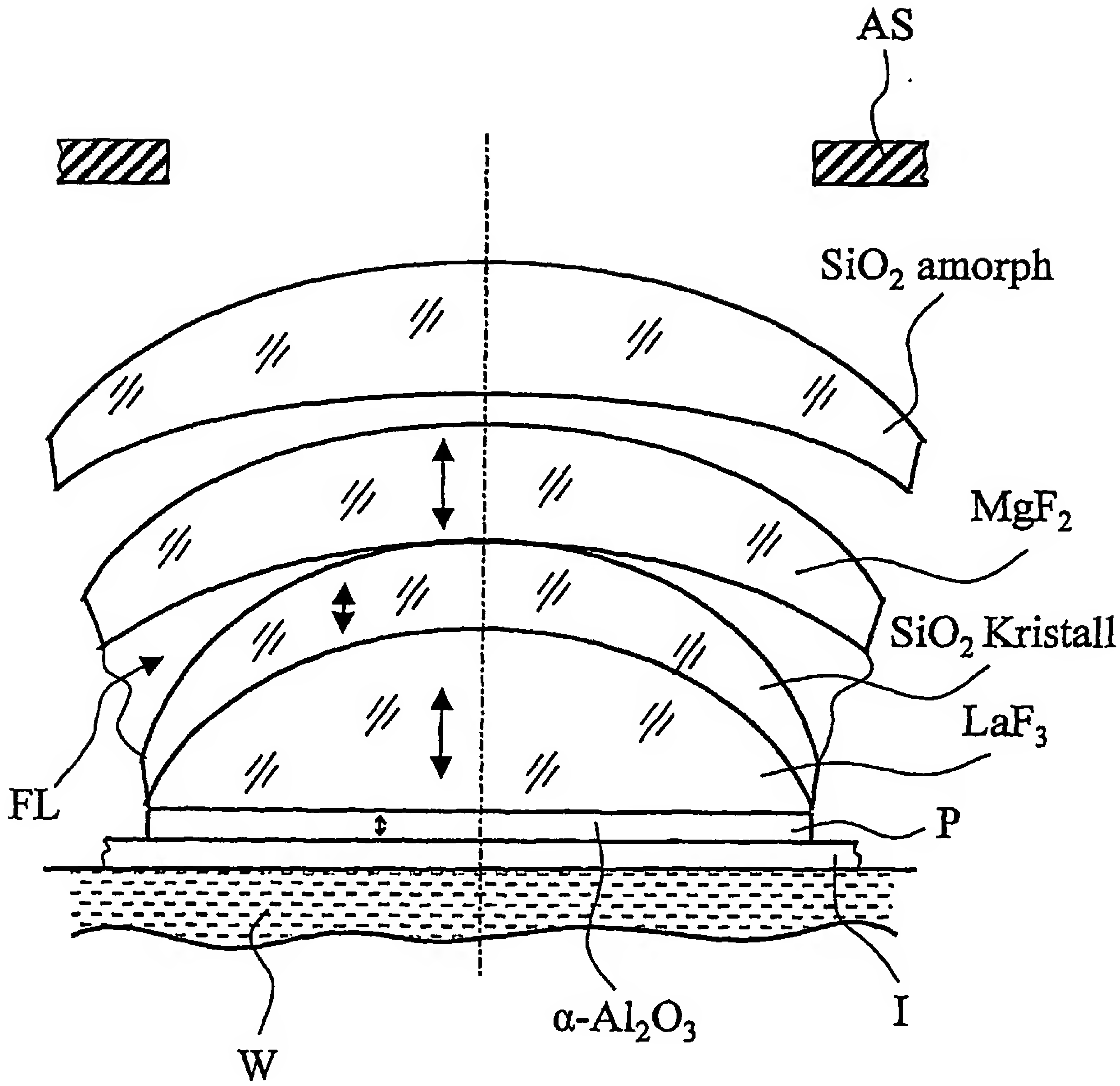
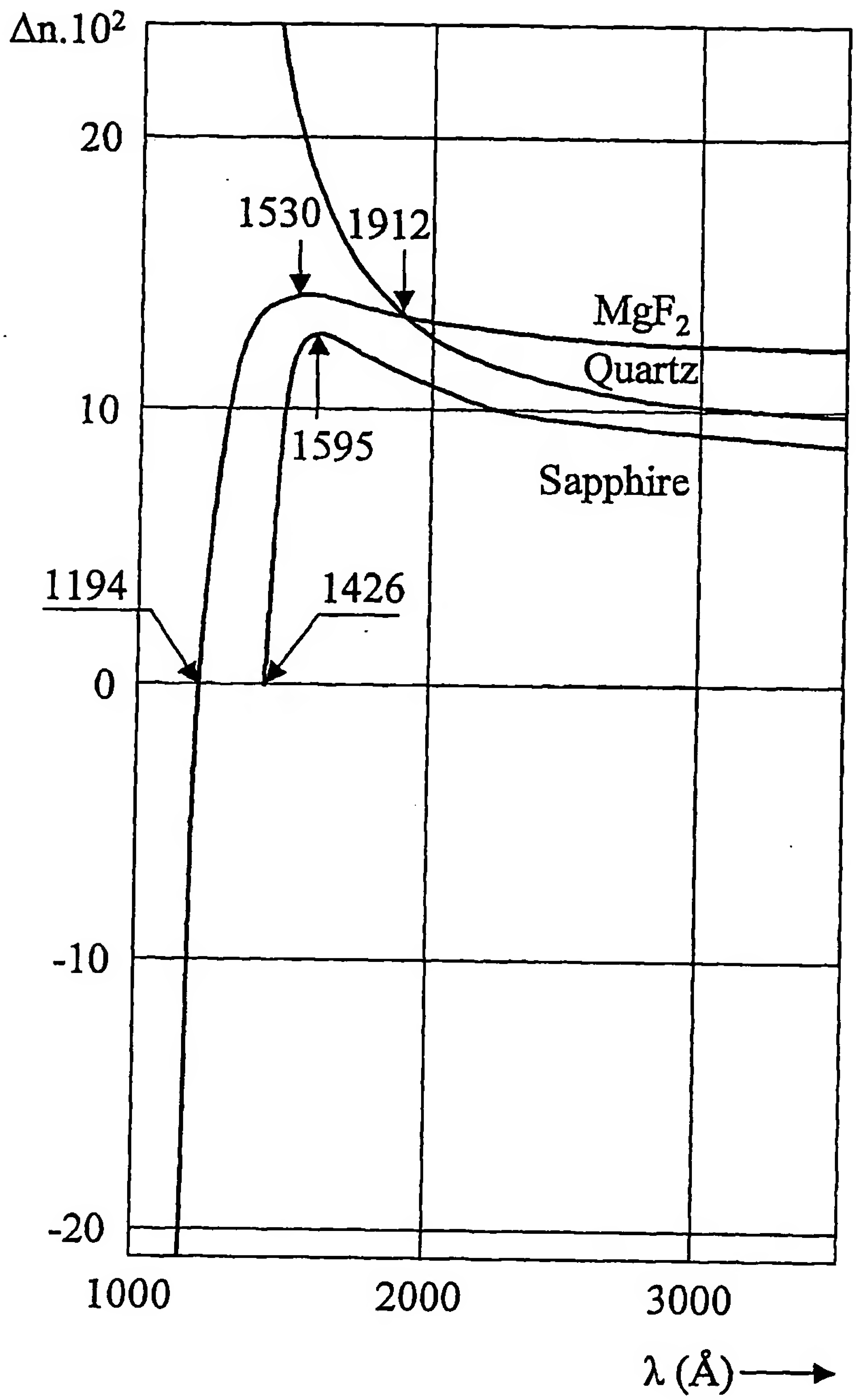


FIG.9


Δn.10²
20
10
0
-10
-20
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1912
1595
1194
1426
MgF₂
Quartz
Sapphire
1000
2000
3000
λ (Å)

FIG.10

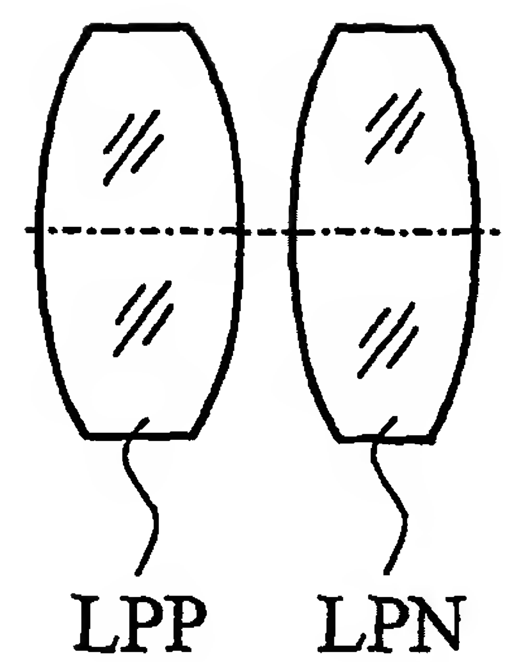


FIG.11

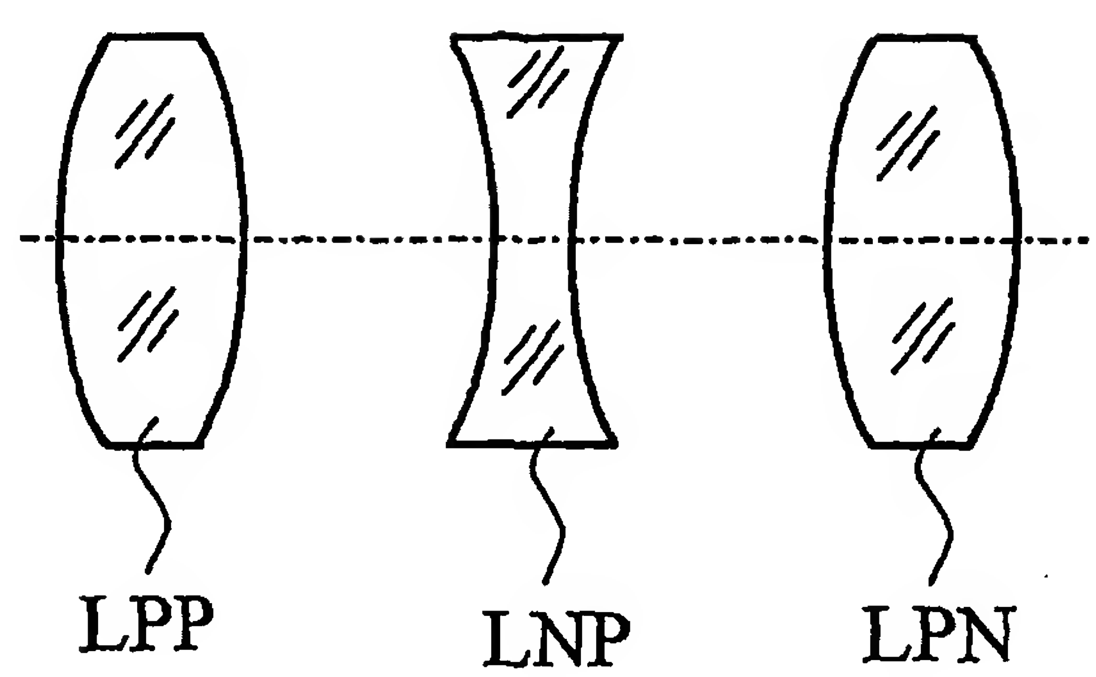


FIG.12

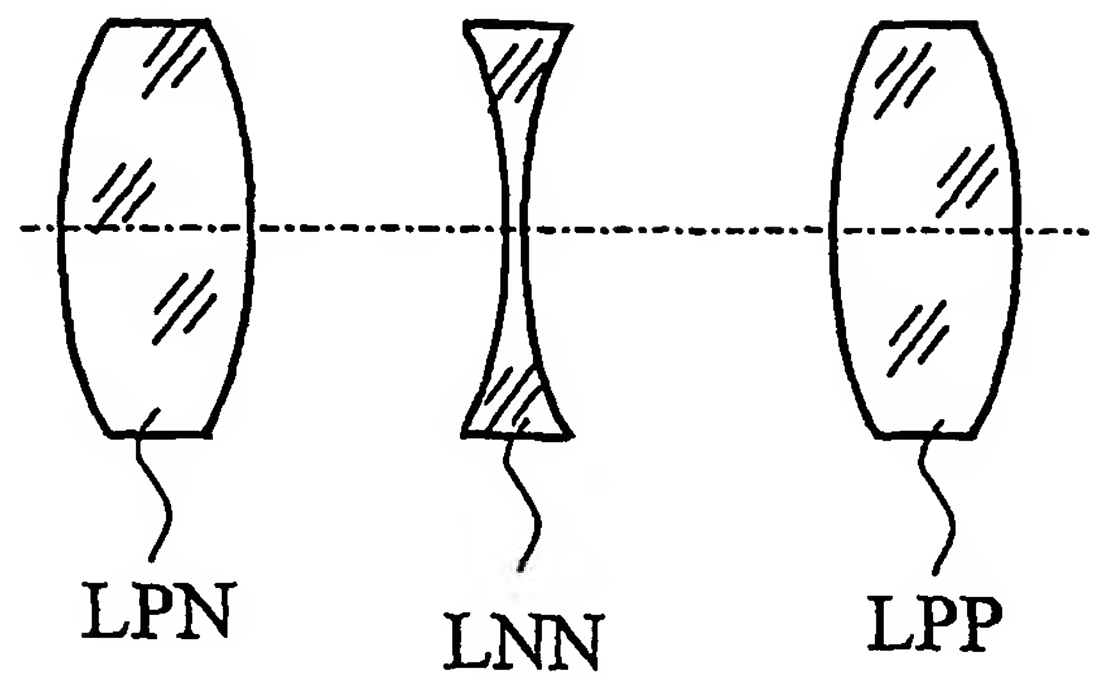
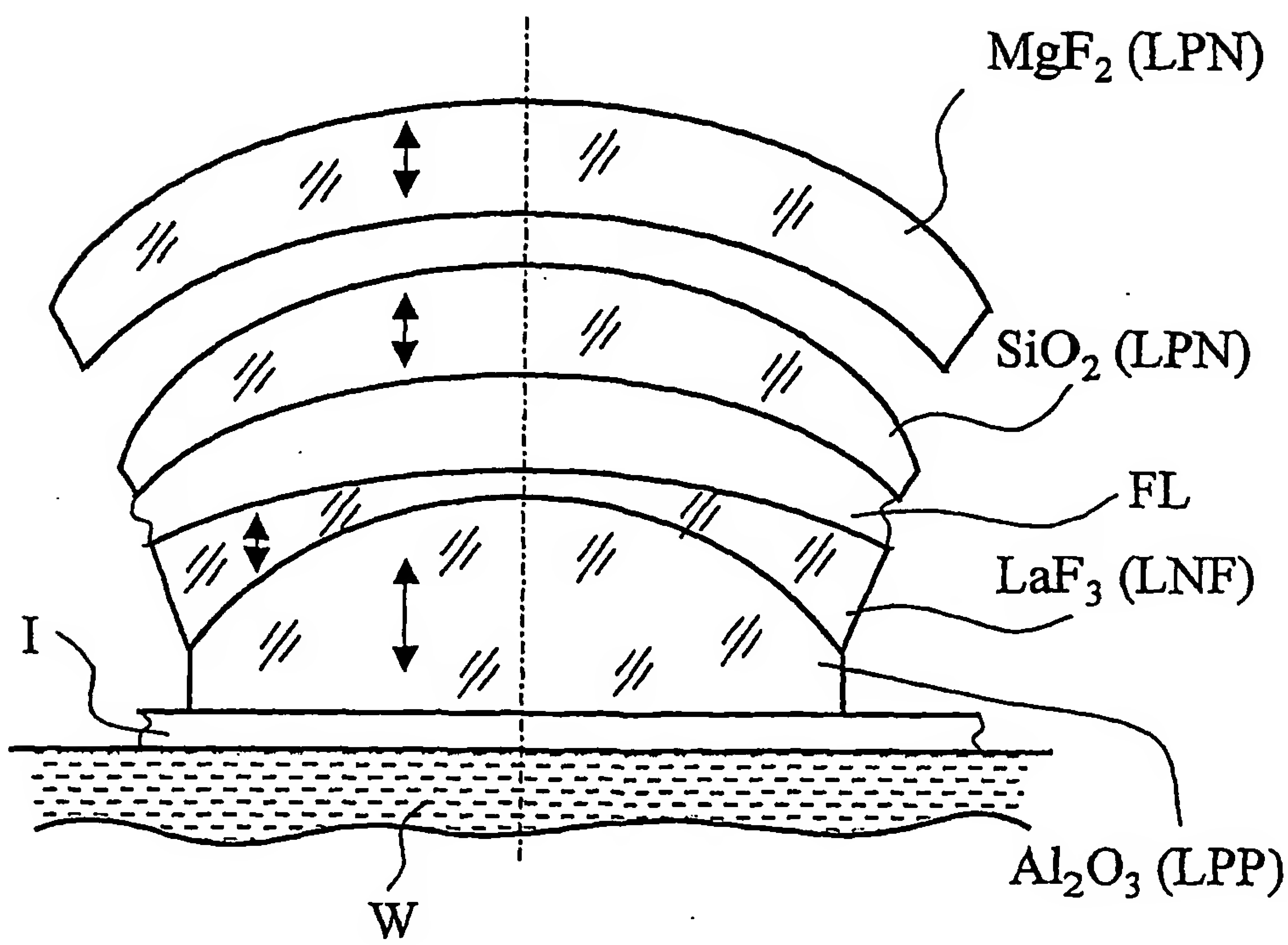


FIG.13



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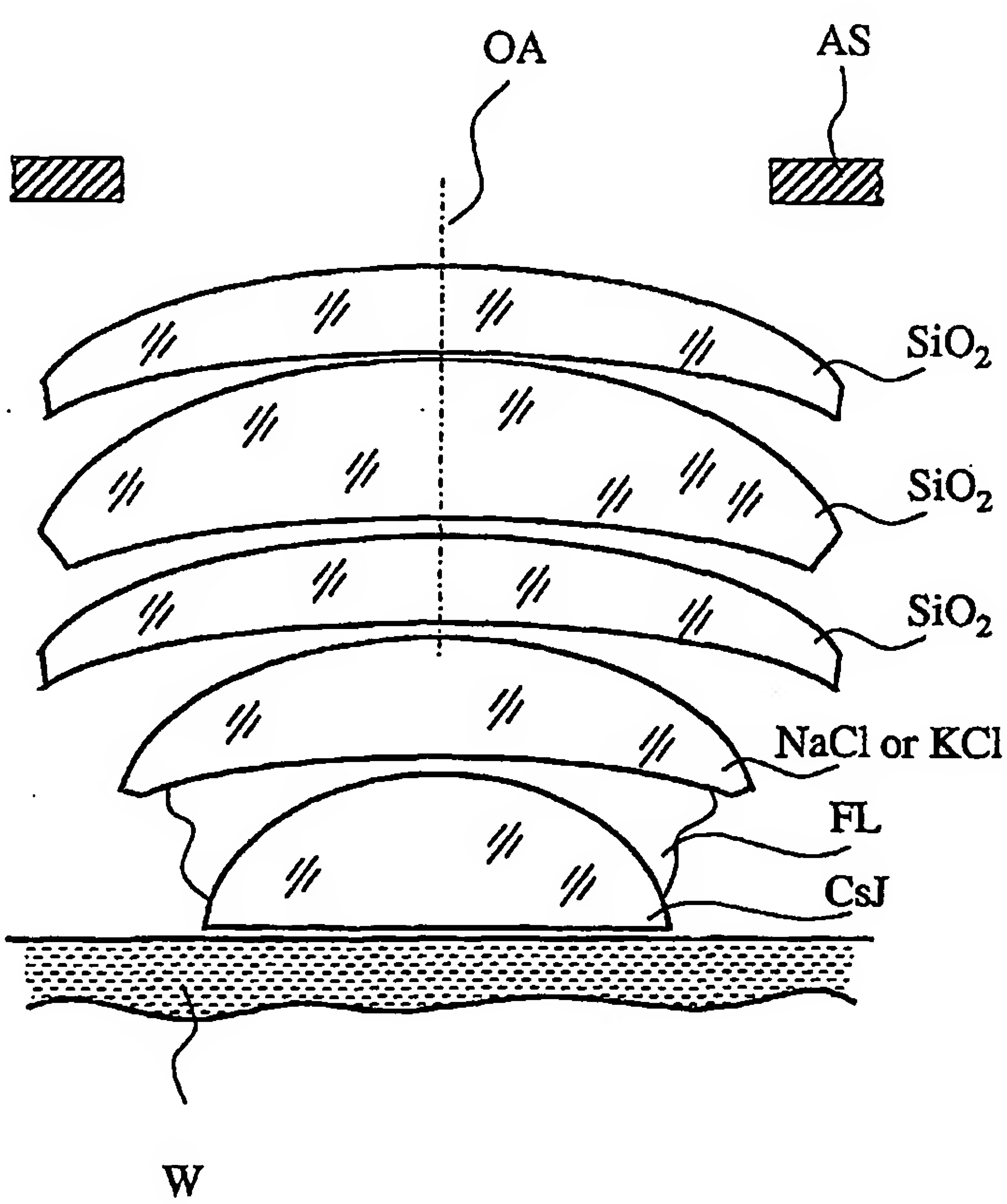
(54) Title: MICROLITHOGRAPHY PROJECTION OBJECTIVE WITH CRYSTAL LENS



(57) **Abstract:** Very high aperture microlithography projection objectives operating at the wavelengths of 248 nm, 193 nm and also 157 nm, suitable for optical immersion or near-field operation with aperture values that can exceed 1.4 are made feasible with crystalline lenses and crystalline end plates P of NaCl, KCl, KI, RbI, CsI, and MgO, YAG with refractive indices up to and above 2.0. These crystalline lenses and end plates are placed between the system aperture stop AS and the wafer W, preferably as the last lenses on the image side of the objective.

WO 2005/059618 A3

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations*

— *of inventorship (Rule 4.17(iv)) for US only*

Published:

— *with international search report*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(88) Date of publication of the international search report: 19 January 2006

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

PCT/EP2004/014290

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03F7/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y X	US 2003/174408 A1 (ROSTALSKI HANS-JUERGEN ET AL) 18 September 2003 (2003-09-18) paragraphs [0025], [0036]; figure 3; table 5	1-10 13,14
P,Y	JOHN H. BURNETT ET AL.: "High Index Materials for 193nm and 157nm Immersion Lithography" INTERNATIONAL SEMATECH, 2 August 2004 (2004-08-02), XP001207229 International Symposium on Immersion & 157 nm Lithography, Vancouver cited in the application the whole document	1-10
X	US 2002/102497 A1 (SPARROW ROBERT W) 1 August 2002 (2002-08-01) paragraph [0010]	13,14

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 August 2005	10.11.05

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Eisner, K

INTERNATIONAL SEARCH REPORT

PCT/EP2004/014290

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 861 148 A (SATO ET AL) 29 August 1989 (1989-08-29) column 1, line 59	1
Y	US 6 025 115 A (KOMATSU ET AL) 15 February 2000 (2000-02-15) column 32, line 51	1
A	EP 0 475 020 A (INTERNATIONAL BUSINESS MACHINES CORPORATION) 18 March 1992 (1992-03-18) page 4, line 57	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2004/014290

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-10, 13, 14

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-10, 13, 14

   prior art: Microlithography projection objective with a numerical aperture larger than 1 and with a lens made from different crystals
   special technical feature: Microlithography projection objective with a lens of crystal materials made from NaCl, KCl, KI, NaI, RbI, CsI, MgO, MgAl204 or Y3Al503.
   problem solved by these technical features:
   high refraction index material increases the numerical aperture of the objective

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2. claims: 11, 12

   special technical feature:
   end plate of a microlithography projection objective made from crystalline magensium oxide.
   problem solved by these technical features:
   protection plate for other optical elements

INTERNATIONAL SEARCH REPORT

PCT/EP2004/014290

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